DESCRIPTION OF PLATES.

Plate 1.

Fig. 26.—7Z½. Slowly cooled from above the liquidus to 345° C. × 300.
Fig. 27.—7Z2. Slowly cooled from above the liquidus to 345° C. × 300.
Fig. 28.—7Z8. Slowly cooled from above the liquidus to 345° C. × 300.
Fig. 29.—7Z10½. Slowly cooled from above the liquidus to 350° C. × 300.
Fig. 30.—7Z12. Annealed at 345° C. × 300.
Fig. 31.—7Z15. Annealed at 345° C. × 300.

Plate 2.

Fig. 32.—9Z12. Slowly cooled from above the liquidus to 350° C. × 100.
Fig. 33.—3Z6. Slowly cooled from above the liquidus to 370° C. × 300.
Fig. 34.—4Z4. Annealed at 300° C. × 300.
Fig. 35.—4Z6. Annealed at 300° C. × 300.
Fig. 36.—4Z7. Annealed at 300° C. × 300.
Fig. 37.—4Z8. Annealed at 300° C. × 300.

The Vacuum Arc Spectra of Sodium and Potassium.

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1. *Introductory.*

In connection with the investigation of spectral series, the need for more accurate measurements of the spectra of the alkali metals has long been felt, especially in the case of the diffuse series and the higher members of the sharp series. When it was found that the "sodium vapour lamp," recently described by Lord Rayleigh,* gave extremely narrow bright lines, such that the term diffuse as applied to one of the series becomes a misnomer, it seemed possible that the desired improvement in the measures of the wave-lengths might be attained by the use of this ideal vacuum arc as a source. Definite improvements in the measures for sodium, as proved by the constancy of the separations of pairs of lines, suggested that a potassium vapour lamp might also be used with probable success. The potassium lamp was much more troublesome than the sodium one, and the lines of the diffuse series were less sharply defined. The new measures of potassium lines, however, are probably more exact than before, and an interesting combination pair, indicating satellites to the diffuse series has been observed.

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* R. J. Strutt, Bakerian Lecture, 'Roy. Soc. Proc.,' A, vol. 96, p. 272 (1919).

2. *Experiments.*

The sodium vapour lamp was excited precisely in the manner described by Lord Rayleigh, being run on a 200-volt circuit, with a current of about 2·5 ampères. When once started it would continue even when the process of evacuation by the Gaede pump was stopped, and heating the bottom bulb by the ring burner done away with, the vapour then being produced by the heat of the arc only; but it was noticed that an increase of vapour pressure caused the lines to become slightly diffuse, and the pump was therefore run continuously during the exposures of the plates.

With potassium, however, continuous evacuation caused considerable difficulty. The vapours rising up by the upward suction of the pump condensed on the sides of the upper bulb and trickled down the stem, rendering it either partially opaque or making a short circuit along the side by the deposited metal. After various trials it was found best to raise the temperature of both the bulbs and stem in such a way that the deposition of metallic potassium was impossible. For this purpose the upper bulb was heated by a ring burner, having a tiny flame, whereas the bottom one was heated by a Bunsen burner intermittently. Even then it was found desirable to decrease the vapour pressure inside the bulb in such a way that the temperature equilibrium was not seriously disturbed by a sudden uprush of the vapour caused by the pump. A side reservoir was therefore connected to the ordinary pump circuit by means of a T-piece. After evacuating the bulb with the pump, the pump circuit was closed, and the side reservoir was kept immersed in liquid air; in this way the pressure could be kept down without making the lamp unstable. The potassium lamp thus required continual attention, but otherwise it was quite satisfactory and gave a sufficiently intense light.

As the bulb was heated it emitted a white light, and the subordinate series lines, as well as the first pair of the principal series lines, appeared to become stronger at the expense of the rest of the members of the principal series, and exactly the opposite took place when it was cooling, the bulb then appearing distinctly bluish. The combination line $1s-2d$ is fairly persistent all the time.

Preliminary photographs were taken with a spectrograph of moderate dispersion, and final measurements were made on photographs taken in the first order, and in some cases in the second order spectrum of the

10-foot concave grating at the Imperial College, giving a dispersion of about 5·6 A.U. per millimetre in the first order.

To get the higher members of the subordinate series it was necessary to give an exposure of about four hours, and in order to guard against possible shifts due to change of temperature or to mechanical displacements during the exposure, the iron comparison spectrum was taken both before and after exposure to the lamp. The appearance of the iron lines in the photograph showed that there was no such shift. The standards of reference were iron lines selected from the table given by Burns.

3. *The Line Spectrum of Sodium.*

The new observations of sodium are compared with those of Kayser* and Zickendraht† in Table I, which includes the separation $\Delta\nu$ of the doublets (in wave numbers), and shows the series to which each of the pairs belongs.

The lines of the sharp series are closely represented by a formula of the Hicks' type, viz.:—

$$\left.\begin{aligned} S_1(m) &= 24476{\cdot}18 \\ S_2(m) &= 24493{\cdot}35 \end{aligned}\right\} - \frac{109678{\cdot}3}{(m+0{\cdot}650835-0{\cdot}013290/m)^2},$$

the constants of which were calculated from the less refrangible components of the pairs 3, 4, and 6. The difference between the observed and calculated wave numbers are also included in the table. The variable parts or "terms" of the other series are then as indicated in the table, their limits being obtained from certain well-established laws of series spectra, according to which the limits of the diffuse series may be taken to be identical with those of the sharp, and the limit of the principal series may be obtained by adding the wave numbers of the first principal lines to the respective limits of the diffuse and sharp series.

4. *The Band Spectrum of Sodium.*

An interesting feature of the sodium vapour lamp was the production of a channelled space emission spectrum, which had its origin only in the bulb of the lamp. These bands always made their appearance when the arc was first started and persisted so long as the bulb did not attain too high a temperature. On removing the ring burner so as to decrease the temperature of the bulb, some of the previous heads only appeared without the entire flutings. A photograph with an instrument of sufficient dispersion to be of value for measurement would have been difficult to obtain on account of

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* Kayser, 'Handbuch der Spectroscopie,' Band VI, p. 116.

† H. Zickendraht, 'Ann. d. Phys.,' vol. 31, p. 233 (1910).

Table I.—Series Lines of Sodium.

Kayser and Runge. λ (Row.)	Δν.	Datta. λ : I.A.	ν (vac.).	Δν.	m.	mp.	$\nu_0 - \nu_c$.
		Principal series: $1s-mp_1$ $1s-mp_2$		$1s = 41449{\cdot}53$			
5890·19 96·16	17·18	5889·965 95·932	16973·35 56·17	17·18	(1)	24476·18 93·36	
		Sharp series: $1p_1-ms$ $1p_2-ms$		$1p_1 = 24476{\cdot}18$ $1p_2 = 24493{\cdot}36$		ms (mean).	
6161·15 54·62	17·22	6160·725 54·214	16227·37 44·54	17·17	(3)	8248·81	*
5153·72 49·19	17·07	5153·645 49·090	19398·34 415·51	17·17	(4)	5077·84	*
4752·19 48·36	16·97	4751·891 48·016	21038·37 55·55	17·18	(5)	3437·81	+0·17
4546·03 42·75	15·89	4545·218 41·671	21995·00 2012·18	17·18	(6)	2481·18	*
Zickendraht. λ : IA.							
4423·2 19·9	16·88	4423·31 19·94	22601·16 18·40	17·24	(7)	1875·00	−0·38
4344·7 41·4	17·49	4344·8 41·5	23009·5 27·1	17·5	(8)	1466·47	−0·50
		Diffuse series: $1p_1-md$ $1p_2-md$		$1p_1 = 24476{\cdot}18$ $1p_2 = 24493{\cdot}36$			
K. & R. (Row.).						md (mean)	
5688·26 82·90	16·59	5688·222 82·675	17575·30 92·47	17·17	(3)	6900·88	
4983·53 79·30	17·04	4982·864 78·608	20063·20 80·34	17·14	(4)	4413·00	
4669·4 65·2	19·28	4668·597 64·858	21413·73 30·89	17·16	(5)	3062·46	
4500·0 494·3	18·19	4497·724 94·266	22227·11 44·25	17·14	(6)	2249·09	
Zickendraht. λ : I.A.							
4393·5 90·1	17·62	4393·45 90·14	22754·77 71·96	17·19	(7)	1721·41	

* Used in calculation of constants.

the low intensity of the bands, and only rough measurements were therefore made with a constant-deviation spectrometer. The heads of the bands appeared in pairs and the bands themselves faded off towards the violet. These bands show very little agreement with the previously recorded absorption or fluorescent bands.* They can, however, be divided into several groups having a nearly constant frequency difference between the heads, thus:—

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* Roscoe and Schuster, 'Roy. Soc. Proc.,' vol. 22, pp. 362–364 (1864); Wood and Moore, 'Astro. Phy. J.,' vol. 18, pp. 94–111 (1903); Wood and Galt, 'Astro. Phy. J.,' vol. 33, pp. 72–80 (1911).

Group I	λ6688—6246	7	equally spaced heads of bands.
Group II	λ6182—5756	9	,, ,,
Group III	λ5554—5340	7	,, ,,
Group IV	λ5281—5101	7	,, ,,

5. *The Line Spectrum of Potassium.*

As in the case of sodium, the new observations of potassium are compared with those of Kayser and Runge* in Table II, which includes the separation $\Delta\nu$ of the doublets (in wave numbers).

The lines of the sharp series may be closely represented by a formula of the Hicks' type, viz.:

$$\left.\begin{array}{l} S_1(m) = 21963{\cdot}06 \\ S_2(m) = 22020{\cdot}84 \end{array}\right\} - \frac{109678{\cdot}3}{(m+0{\cdot}821947-0{\cdot}054486/m)^2},$$

for which the less refrangible components of the pairs 5, 6, and 7 were used in the calculation of constants. The residuals are shown in Table II. From the limits $1p_1$, $1p_2$, thus determined, the limit of the principal series was also derived in the usual way, and the variable parts or "terms" *mp, ms,* and *md* of all the lines were then calculated as shown in the table.

6. *The Second Principal Pair of Lines.*

In connection with combination terms involving the second principal pair of potassium, Paschen found it necessary to adopt wave-lengths some tenths of an Ångström higher than those measured by Kayser and Runge, and it was therefore thought desirable to investigate this pair more completely.

Several photographs were taken of this pair as given by the arc in air as well as in the vacuum bulb. The measures obtained from different photographs of the bulb were in close agreement with each other. But those obtained from the arc in air differed according as the lines were reversed or unreversed. In ordinary circumstances the lines of the principal series are strongly reversed, but by feeding the arc sparingly with potassium bicarbonate it was found possible to obtain plates with the lines unreversed. Measurements showed that when the reversal was broad the wave-length of the centre of reversal was about 0·1 A.U. higher than that of the unreversed line, indicating that reversal takes place unsymmetrically.

A further interesting point observed was that when the reversal is narrow the centre has a distinctly lower value than when it is broad, suggesting that

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* H. Kayser, 'Handbuch der Spectroscopie,' Band V, p. 634.

Table II.—Series Lines of Potassium.

Principal series: $\left.\begin{array}{l}1s-mp_1\\1s-mp_2\end{array}\right\}$ $1s = 35005·88$

Kayser and Runge.		Datta.					
λ (Row.).	Δν.	λ: I.A.	ν (vac.).	Δν.	m.	$mp_{1,2}$.	$\nu_o-\nu_c$
—	—	7664·94* 99·01*	13042·82 12985·04	57·78	(1)	21963·06 22020·84	
4044·29 47·36	18·76	4044·140 47·201	24720·18 24701·49	18·69	(2)	10285·70 10304·39	
3446·49 47·49	8·41	3446·722 47·701	29004·70 28996·55	8·15	(3)	6001·18 6009·33	
3217·27 17·76	4·73	3217·01 17·50	31075·88 71·05	4·83	(4)	3930·00 3934·83	

Sharp series: $1p_1-ms$ $1p_1 = 21963·06$
$1p_2-ms$ $1p_2 = 22020·84$

						ms (mean).	
6938·8 11·2	57·56	6939·50 11·80	14406·35 64·10	57·80	(3)	7556·71	+0·50
5802·01 782·67	57·64	5802·16 782·77	17230·21 87·97	57·77	(4)	4732·85	+0·11
5340·08 23·55	58·14	5339·670 23·228	18722·56 80·40	57·84	(5)	3240·50	†
5099·64 84·49	58·42	5099·180 84·212	19605·54 63·28	57·74	(6)	2357·52	†
4956·8 43·1	55·91	4956·043 41·964	20171·61 229·34	57·63	(7)	1791·45	†
—	—	4863·61 49·88	20555·16 613·33	58·17	(8)	1407·90	+0·29
—	—	4800·16 786·89	20826·82 984·58	57·76	(9)	1136·24	−0·55
—	—	4754·5 41·6	21026·7 21084·0	57·3	(10)	936·36	−1·07

Diffuse series: $1p_1-md$ $1p_1 = 21963·06$
$1p_2-md$ $1p_2 = 22020·84$

						md (mean).
5832·23 12·54	58·08	5832·31 12·71	17141·13 98·91	57·78	(4)	4821·93
5359·88 43·35	57·72	5359·521 42·974	18653·20 711·00	57·80	(5)	3309·86
5112·68 097·75	57·28	5112·204 097·144	19555·61 613·38	57·77	(6)	2407·45
4965·5 52·2	54·09	4965·038 50·816	20135·23 93·08	57·85	(7)	1827·83
—	—	4869·70 56·03	20529·46 87·23	57·77	(8)	1433·60
—	—	4805·19 791·08	20805·03 66·33	61·30	(9)	1158·03
—	—	4759·31 45·58	21005·58 66·38	60·80	(10)	957·48

Combination.			ν (cal.).	Series.
4642·172 41·585	21535·62 38·36	2·74	21535·46	$1s-2d$ $1s-2d'$

* These values have been taken from Meggers.
† Used in calculation of constants.

the reversed line also shrinks unsymmetrically. The same thing is suggested by the sharp and diffuse series lines emitted by the vacuum bulb, for they shrink into fine lines which have in some cases several tenths of an Ångström unit lower value than those given by Kayser for the arc in air.

The following table shows the various measures of the pair :—

Table III.

Source.	λ I.A. p_1 (2).	λ I.A. p_2 (2).
Vacuum arc (2nd order)	4044·140	4047·201
,, ,, (1st ,,)	4044·146	4047·206
Arc in air, unreversed	4044·160	4047·230
,, fine reversal	4044·168	4047·239
,, broad reversal	4044·274	4047·342

7. *The Combination Pair* $1s$–$2d$, $1s$–$2d'$.

The close pair of narrow bright lines at 4642·172, 4641·585 has previously observed only as a single line but has been recognised as the combination $1s$–$2d$. The occurrence of a *pair* of lines at once suggests the combinations $1s$–$2d$ and $1s$–$2d'$; or in other words that there is a satellite to the line d_1 (2) of the diffuse series, with a separation of 2·74 in wave number. This *d* (2) pair is in the infra-red, at wave-lengths 11771·73, 11689·76 according to Paschen, and the satellite has not yet been observed. The fact that the less refrangible component of the combination pair is the stronger would seem to indicate that the satellite to d_1 (2) is abnormally placed on the more refrangible side of the chief line. The probable existence of a satellite to d_1 (2) further suggests that the associated fundamental series, which has its lines in the far red and infra-red, should also consist of pairs, with separation 2·74, but these lines have not yet been recorded as doublets.

It does not seem possible to trace any definite relation between the satellite separation of potassium and those of rubidium and cæsium. The existence of satellites in the diffuse series of cæsium is well established, and their separations in successive terms of the series appear to be quite normal. In the case of rubidium, however, though an apparent satellite with a separation of 2·93 has been observed in the second member of the series *d* (3), there is no record of a satellite to the infra-red member *d* (2). Prof. Hicks* doubts the reality of the satellite to *d* (3), and the absence of a satellite to *d* (2) is rendered probable by the fact that the combination $1s$–$2d$ of rubidium (λ5165·18) only appears as a single line.

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* Hicks, 'Phil. Trans.,' A, vol. 210, pp. 57–111 (1910).

8. *Sodium and Potassium Lines in the Solar Spectrum.*

Sodium is represented in the Sun by several coincidences, among which the most important lines are the lines D_1 and D_2 which constitute the first pair of the principal series. A recent publication of the Allegheny Observatory* shows that the lines with wave-lengths 8183·30 A. and 8194·82 A. which form the first pair of the diffuse series, are prominent in the infra-red solar spectrum. The new measures of sodium suggest additional identification of solar lines as shown in the following table:—

Table IV (*a*).—Sodium Lines in the Sun.

Series.	Rowland (λ).	Intensity.	Datta (λ.I.A.).	Correction to International scale.	Remarks.
s_1 (3)	6160·956	3	6160·725	+0·22	Previously recorded, but the new measures give much better agreement.
s_2 (3)	54·438	2	54·214		
d_1 (3)	5688·436	6	5688·222	+0·22	
d_2 (3)	82·869	5	82·675		
s_1 (4)	5153·848	000	5153·645	+0·18	
s_2 (4)	49·267	000	49·090		C? (Rowland).
d_1 (4)	4982·994	2	4982·864	+0·18	
d_2 (4)	78·785	3	78·608		Masked by Fe.
d_1 (5)	4668·749	1	4668·597	+0·17	
d_2 (5)	—	—	64·858		Masked by Cr.
d_1 (6)	4497·842	0	4497·724	+0·17	
d_2 (6)	94·356	00	94·266		

The existence of potassium in the Sun was considered uncertain until recently, because its presence was indicated by only one faint line, 4044·140 A. [$p_1(2)$]. The presence of the first pair of principal lines 7664·94 A. and 7699·01 A. was established in the course of the present investigation, and confirmatory evidence has been published by Meggers.†

The less refrangible member of the first pair, 7699·01 A., is unmistakably in the Sun and shows a shift at the Sun's limb of about 0·06 A. as compared with the centre, on a solar rotation plate kindly lent by Prof. Sampson, the calculated shift being about 0·058 A. The second line of the pair, 7664·94 A., is masked by a strong broad line in the A band of oxygen, and, although the rotation shift did not separate it in the photograph, it was found to produce a distinct broadening of the oxygen line by about 0·04 A. Lester's‡ value of this oxygen line is 7665·14 A., and, as it has a breadth of about 0·26 A., the potassium line is to be expected at

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* Meggers, 'Publications of the Allegheny Observatory,' vol. 6, No. 3.

† Meggers, *loc. cit.*

‡ Lester, 'Astro. Phy. J.,' vol. 20, p. 81.

7665·14+0·13−7665·25 = 0·02 A., inward from the edge. Consequently, a shift of 0·06 A. will clearly broaden the line by 0·04 A. Meggers has obtained quite definite evidence on this point, by observing the notched appearance of the oxygen line in the juxtaposed spectra of the two limbs.

Other lines of potassium possibly represented in the solar spectrum are shown in the following table:—

Table IV (*b*).—Potassium Lines in the Sun.

Series.	Rowland (λ).	Intensity.	Datta (λ.I.A.).	Correction to International scale.	Remarks.
p_2 (1)	7699 ·297	—	7699 ·01	+0 ·28	Values taken from Meggers.
p_1 (1)	65 ·248	—	64 ·94		
d_1 (3)	6965 ·320	000	6965 ·0	+0 ·25	Values taken from Saunders.
d_2 (3)	36 ·290	0000	36 ·0		
d_1 (4)	5832 ·490	000	5832 ·31	+0 ·22	
d_2 (4)	12 ·942	0000	12 ·71		
d_1 (5)	5359 ·714	000	5359 ·521	+0 ·19	
d_2 (5)	43 ·148	0000	42 ·974		
p_2 (2)	4047 ·338	00	4047 ·201	+0 ·15	Previously recorded.
p_1 (2)	44 ·294	0	44 ·140		
p_1 (3)	46 ·857	000	3446 ·722	+0 ·14	

9. *Summary.*

1. The wave-lengths of the sharp and diffuse series of lines of sodium and potassium have been carefully measured in a source giving well-defined lines.

2. Channelled-space emission bands have been observed in the sodium vapour lamp, and their heads approximately measured.

3. The combination line $1s-2d$ in potassium has been resolved into a pair, and their wave-lengths measured.

4. The presence of potassium in the Sun has been established, and some additional sodium lines have been identified with solar lines.

In conclusion, I beg to thank Prof. A. Fowler, F.R.S., for his taking helpful interest in the work, Lord Rayleigh for the use of his lamp, and Prof. Sampson for kindly lending me a Solar rotation plate.